BNL-77971-2007-JA

AN EXAMINATION OF KÖHLER THEORY RESULTING IN AN ACCURATE EXPRESSION FOR THE EQUILIBRIUM RADIUS RATIO OF A HYGROSCOPIC AEROSOL PARTICLE VALID UP TO AND INCLUDING RELATIVE HUMIDITY 100%

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May 2007

Revised: August 2007

Submitted to
J. Geophys. Res.

Environmental Sciences Department/Atmospheric Sciences Division

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An Examination of Köhler Theory Resulting in an Accurate Expression for the Equilibrium Radius Ratio of a Hygroscopic Aerosol Particle Valid up to and Including Relative Humidity 100%

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Keywords: Köhler theory, Growth factor, Relative humidity, Kelvin effect, Hygroscopicity, Osmotic coefficient

Abstract

The equilibrium hygroscopic behavior of an aqueous solution drop is investigated using the Köhler model to relate the radius ratio $\xi \equiv r/r_{\mathrm{dry}}$, where r_{dry} is the volume-equivalent dry radius, and the fractional relative humidity h. The Köhler equation is derived and results obtained from it are presented for three situations: when the effect of surface tension can be neglected, for $h = 1$, and for cloud-drop activation. The exact solution to this equation is presented, as is an accurate approximate solution for $h < 1$ that yields insight into the dependences of the equilibrium radius on relative humidity, surface tension, and dry radius. The approximations made in the derivation of the Köhler equation are examined, errors in quantities obtained from this equation are quantified, and the so-called Debye approximation is introduced which allows accurate parameterization of these errors as a function of r_{dry}. Errors in the radius ratio at activation obtained from the Köhler equation are up to 20% for ammonium sulfate solution drops of the size that typically form cloud drops. Attempts to extend the Köhler model to higher concentrations are examined, and it is seen that the primary cause of inaccuracy in the model is the assumption that the practical osmotic coefficient is unity. Based on this analysis, a simple two-parameter expression is presented for the equilibrium radius ratio as a function of h and r_{dry} that is accurate over a wide range of r_{dry} and for h up to and including unity.

Nomenclature

a	parameter in expression for radius ratio
a_{w}	water activity
A_ϕ	constant, ≈ 0.392 mol$^{1/2}$ kg$^{-1/2}$ at 25ºC
b	parameter in expression for radius ratio
B	parameter characterizing hygroscopicity
c	parameter that depends on solute, $\equiv [\nu(M_{\mathrm{w}}/M_{\mathrm{s}})(\rho_{\mathrm{dry}}/\rho_{\mathrm{w}})]^{1/3}$
c_1	constant
C_1, C_2, C_3, C_4	constants in expression of *Gerber* [1985]
d	parameter that depends upon solute, $\equiv \lvert z_+ z_- \rvert (I/m)^{1/2}$
F_h	factor for fractional relative humidity term, $\equiv -\ln h/(1 - h)$
F_{K}	factor for Kelvin term, $\equiv \xi_\sigma/\xi_{\sigma,0}$
F_{R}	factor for Raoult term, $\equiv \phi/[1 - (\rho_{\mathrm{dry}} V_\phi/M_{\mathrm{s}})/\xi^3]$
F_ξ	factor comprising F_{R}, $\equiv 1/[1 - (\rho_{\mathrm{dry}} V_\phi/M_{\mathrm{s}})/\xi^3]$
F_ϕ	factor comprising F_{R}, $\equiv \phi$
h	fractional relative humidity, $\equiv$ RH/100%
h_{act}	fractional relative humidity at activation
I	ionic strength of solution, mol kg^{-1}
K	parameter that depends upon solute
m	molality, mol kg^{-1}
m_{dry}	dry mass of (anhydrous) solute
M_{s}	molar mass of solute
M_{w}	molar mass of water, $\approx$ 0.018 kg mol^{-1}
n	constant
r	drop radius
$\breve{r}$	characteristic length for radius at activation, $\equiv r_{\sigma,0}/(3c^3)$
$\hat{r}$	characteristic length for supersaturation at activation, $\equiv 2^{2/3} r_{\sigma,0}/(3c)$
r_1	radius at $h = 1$
$\tilde{r}_1$	characteristic length for fractional error in r_1 obtained from Köhler model
r_{act}	radius at activation
$\tilde{r}_{\mathrm{act}}$	characteristic length for fractional error in r_{act} obtained from Köhler model
r_{dry}	volume-equivalent dry radius, $\equiv [3m_{\mathrm{dry}}/(4\pi\rho_{\mathrm{dry}})]^{1/3}$
$r_{\mathrm{dry,c}}$	critical value of r_{dry} for activation
r_σ	characteristic length scale for Kelvin effect, $\equiv 2\bar{v}_{\mathrm{w}}\sigma/(RT)$
$r_{\sigma,0}$	value of r_σ evaluated for pure water, $\approx$ 1.1 nm
R	gas constant, $\approx$ 8.3 J K^{-1} mol^{-1}
RH	relative humidity, %
s	supersaturation, $\equiv h - 1$
$\tilde{s}$	characteristic supersaturation for fractional error in $r_{\mathrm{dry,c}}$
s_{act}	supersaturation at activation
T	absolute temperature, K

$\bar{v}_w$	partial molal volume of water in solution ($=M_w/\rho_w$ for pure water)
V_ϕ	apparent molal volume of solute in solution
z	scaled radius ratio in Köhler equation for $h < 1$, $\equiv [(r/r_{dry})/c](1-h)^{1/3}$
z_0, z_1	terms in expression for z in Köhler equation for $h < 1$
z_+, z_-	magnitudes of charges of the positive and negative ions, respectively, into which electrolyte dissociates in solution
α	function of h in parameterization of radius ratio
β	function of h in parameterization of radius ratio
Δs	fractional error in supersaturation calculated by Köhler model
Δs_{act}	value of Δs at activation
$\Delta\xi$	fractional error in radius ratio calculated by Köhler model
$\Delta\xi_1$	value of $\Delta\xi$ at $h = 1$
$\Delta\xi_{act}$	value of $\Delta\xi$ at activation
ε	scaled Kelvin factor in Köhler equation for $h < 1$, $\equiv [(r_{\sigma,0}/r_{dry})/c]/(1-h)^{2/3}$
κ	hygrocopicity parameter of *Petters and Kreidenweis* [2007]
ν	number of ions into which a molecule of solute dissociates
ν_+, ν_-	number of positive and negative ions, respectively, into which a molecule of solute dissociates
ξ	radius ratio relative to volume-equivalent dry radius, $\equiv r/r_{dry}$
ξ_1	radius ratio at $h = 1$
ξ_{act}	radius ratio at activation
ξ_σ	ratio of characteristic length scale for Kelvin effect to r_{dry}, $\equiv r_\sigma/r_{dry}$
$\xi_{\sigma,0}$	value of ξ_σ for pure water
σ	surface tension of solution-air interface
ρ	density of solution
ρ_{dry}	density of (anhydrous) solute
ρ_w	density of pure water, $\approx 1.0{\cdot}10^3$ kg m^{-3}
ϕ	practical osmotic coefficient
$\bar{\phi}$	constant value of ϕ assumed in expression for radius ratio
ϕ_1	value of ϕ at $h = 1$
ϕ_{act}	value of ϕ at activation

1. Introduction

Many atmospheric aerosol components of interest are hygroscopic, meaning that a solution drop composed of one of these substances readily takes up water with increasing fractional relative humidity h (≡RH/100%). Consequently, the equilibrium radius r of such a drop exhibits a strong dependence on h. As r is an intrinsic property of an aerosol particle, controlling its dynamics, light-scattering, dry deposition, and the like, knowledge of this dependence is thus necessary to understand and parameterize many aerosol processes, both in the atmosphere and in the laboratory.

The radius of an aqueous solution drop containing a specified mass of given solute is an unambiguous measure of the solute concentration, and at a given temperature uniquely determines important properties such as water activity, index of refraction, density, and surface tension. This concentration can thus be parameterized by the equilibrium radius ratio $\xi \equiv r/r_{\mathrm{dry}}$, where the volume-equivalent dry radius r_{dry} is defined in terms of the mass of solute in the drop m_{dry} and the bulk dry density of the (anhydrous) solute ρ_{dry} by $r_{\mathrm{dry}} = [3m_{\mathrm{dry}}/(4\pi\rho_{\mathrm{dry}})]^{1/3}$. This volume-equivalent dry radius is not necessarily equal to the physical radius of a dried particle, or to a measured quantity such as the mobility radius (because of nonsphericity of the particle, the presence of residual water either within the particle or on its surface, or the presence of voids which would result in the density being different from that of the bulk solute); nevertheless, r_{dry} is a physically meaningful measure of the size of such a particle, and together with specification of ρ_{dry} provides an unambiguous measure of the solute mass [*Lewis*, 2006].

When exposed to a given relative humidity, a hygroscopic aerosol particle will exchange water substance, thus changing its radius (and radius ratio), until the vapor pressure of water adjacent to the drop is in equilibrium with this relative humidity. At a given temperature, this equilibrium vapor pressure, and thus the equilibrium radius ratio ξ, is controlled by two factors: vapor-pressure lowering due to the presence of the solute, the Raoult effect [*Raoult*, 1887], and the increase in equilibrium vapor pressure from that of the bulk solution caused by the curvature of the drop, the Kelvin effect [*Thomson*, 1871].

The Raoult effect reduces the water activity of the solution a_w from that of pure water (unity) by an amount that increases with increasing solute concentration. The dependence of a_w on solute concentration has been measured for many substances using bulk solutions that are undersaturated with respect to the solute, and using solution drops supersaturated with respect to the solute that are suspended in an electrodynamic balance or are in a hygroscopic tandem differential mobility analyzer. For dilute solutions the vapor-pressure lowering is nearly directly proportional to the concentration (Raoult's Law), although for higher concentrations this relationship becomes increasingly less accurate.

The Kelvin effect results in an increase in the equilibrium vapor pressure of water above an aqueous solution drop by the factor $\exp\{2\bar{v}_w \sigma/(RTr)\}$, where $\bar{v}_w$ is the partial molal volume of water in the solution, σ the surface tension of the solution-air interface, R the gas constant, and T the absolute temperature [*Tang*, 1976]. A characteristic length scale for the Kelvin effect can thus be defined [*Lewis*, 2006] by $r_\sigma \equiv 2\bar{v}_w \sigma/(RT)$, allowing the Kelvin effect to be parameterized in terms of the ratio of $\xi_\sigma \equiv r_\sigma/r_{dry}$ and ξ. The quantities $\bar{v}_{\mathrm{w}}$ and σ, and thus r_σ, depend on the solute and its concentration, and for most inorganic salts of atmospheric interest r_σ is an increasing function of solute concentration and thus a decreasing function of a_{w}, or of h for a given r_{dry} (although for organic solutes this might not be so). The quantity $r_{\sigma,0}$ is defined as the value of r_σ calculated with $\bar{v}_{\mathrm{w}}$ and σ taken as their values at infinite dilution (that is, of pure water), and the quantity $\xi_{\sigma,0}$ is defined similarly as $\xi_{\sigma,0} \equiv r_{\sigma,0}/r_{\mathrm{dry}}$. Both r_σ and $r_{\sigma,0}$ depend weakly on temperature, but over a wide range of temperatures $r_{\sigma,0}$ is approximately equal to 1.1 nm, typically varying by less than 10% from this value between 0 and 25ºC.

The relation between the fractional relative humidity h in equilibrium with an aqueous solution drop with radius ratio ξ and corresponding water activity a_{w}, which incorporates both the Raoult effect and the Kelvin effect, is given by

$$h = a_{\mathrm{w}}\left(\xi\right)\exp\left\{\frac{\xi_\sigma\left(\xi\right)}{\xi}\right\}, \tag{1}$$

where the dependences of both a_{w} and ξ_σ on concentration are explicitly written as dependences on ξ. This relation, for a given r_{dry}, is essentially a transformation between h and a_{w}. Contours of constant h as a function of a_{w} and r_{dry}, and contours of constant a_{w} as a function of h and r_{dry}, are shown in Fig. 1 for solution drops of ammonium sulfate and sodium chloride (as surface tension measurements have not been reported for solutions that are supersaturated with respect to the solute, corresponding to water activities below 0.80 for ammonium sulfate and 0.75 for sodium chloride, values of r_σ in this range of a_{w} are determined from extrapolation of a linear fit of r_σ vs. a_{w} for solutions that are undersaturated with respect to the solute, as described by *Lewis*, 2006). For large drops h and a_{w} are nearly equal, but with decreasing r_{dry} a given value of a_{w} corresponds to larger values of h because of the increasing importance of the Kelvin effect, permitting drops to remain in equilibrium at values of h greater than unity.

As ξ_σ is determined solely by ξ and r_{dry} for a given solute and temperature, Eq. (1) can be formally expressed as $h = h(\xi, \xi_\sigma)$. However, it is often desirable to determine ξ for a given value of h, as the relative humidity is typically the controlling variable. Thus it is necessary to invert the above relation for h to yield an expression of the form $\xi = \xi(h, \xi_\sigma)$, where the dependences on surface tension and r_{dry} (i.e., the Kelvin effect) are contained only in ξ_σ. For situations in which the Kelvin effect is negligible, such as sufficiently large drops at values of h not extremely close to unity (referred to as bulk solution drops throughout this paper), the exponential factor in Eq. (1) is very nearly unity and to good approximation $h = a_{\mathrm{w}}(\xi)$, which can be inverted (at least in principle) to yield a relation of the form $\xi = \xi(a_{\mathrm{w}}) = \xi(h)$. Determination of such an expression for ξ for situations in which the Kelvin effect is not negligible is not in general possible, but if this effect is slight it can be treated as a small perturbation, and an approximation that is accurate over a wide range of fractional relative humidities and particle sizes for several substances of atmospheric interest is given by

$$\xi\left(h,\, r_{\mathrm{dry}}\right) \approx \xi\left(h\right) - \frac{h/\left(1-h\right)}{3\left(r_{\mathrm{dry}}/\mathrm{nm}\right)} \tag{2}$$

[*Lewis*, 2006]. With increasing h, however, this approximation becomes increasingly inaccurate, and the perturbation analysis ultimately fails.

An alternative approach to determining ξ for given h and r_{dry} is discussed below, and a simple but accurate expression is presented for ξ as a function of h and ξ_σ that is valid up to and including $h = 1$. Such an expression has several advantages: it allows insight into the dependences of the radius, or radius ratio, on relative humidity and dry solute mass, provides a formulation by which hygroscopic growth data can be parameterized, and permits ready evaluation of the radius of a drop with given mass of a known solute without the need for more complicated models in which it must be calculated iteratively and in which the dependences on relative humidity and dry solute mass are not clearly identified. Thus, this expression may be useful for global climate models, for instance, where large spatial scales preclude the need for extreme accuracy and where computational expense is a consideration.

2. Köhler Model

A widely used model relating the fractional relative humidity h and the equilibrium radius ratio ξ of an aqueous solution drop containing a given mass of solute characterized by r_{dry} is that proposed by *Köhler* [1921]. This model, which accounts for both the Raoult effect and the Kelvin effect, is standard textbook fare and has proven quite successful in explaining many of the phenomena associated with hygroscopic growth that occur at relative humidities near or above 100%, such as cloud drop activation. Additionally, it is the basis for more complicated models often purported to be valid over a wider range of relative humidities, and for those that include effects of insoluble inclusions and other substances [e.g., *McKinnon*, 1969; *Junge and McLaren*, 1971; *Hänel*, 1976; *Pruppacher and Klett*, 1978; *Chen*, 1994; *Shulman et al.*, 1996; *Laaksonen et al.*, 1998; *Li et al.*, 1998; *Hori et al.*, 2003; *Kulmala et al.*, 2004; *Tammet and Kulmala*, 2005]. Because of its importance and widespread application, examination of this model to determine the range of conditions under which it may be expected to yield accurate results is warranted. Hence it is necessary to consider the approximations inherent in the model and the assumptions required, their satisfaction, and the consequences of the failure of them to be satisfied, to determine which approximation limits accurate extension of the model to higher concentrations, and to quantify the errors resulting from its application.

In the following sections the basic Köhler model is examined and the Köhler equation, expressed in terms of dimensionless quantities, is derived. Results obtained from this model are briefly reviewed, and its accuracy in several situations is quantified. A theoretical explanation for the errors resulting from the model in the so-called Debye limit is given in Appendix A. Although the analysis presented below is applicable for any inorganic solute that dissociates in solution, specific examples are provided for aqueous solution drops of two common atmospheric constituents, ammonium sulfate and sodium chloride, at 25ºC. Not only are these two substances important in their own right, but results for them provide estimates for the magnitude of values for other substances and some indication of the range of values that might be expected. Although measurements of water activities over the entire range considered here have not been reported (for example, measurements have not been reported for water activities of ammonium sulfate solutions with molality less than 0.13 mol kg^{-1}, corresponding to water activities greater than 0.995), formulations of water activity that extend to lower concentrations (i.e., higher water activities) based on theory and on measurements of other physical and chemical properties have been developed which are expected to be accurate. The values used here are calculated from the formulations presented in *Clegg et al.* [1995] for ammonium sulfate solutions and *Clegg et al.* [1997] for sodium chloride solutions.

2.1 Derivation of Köhler equation

The water activity a_w of an aqueous electrolytic solution containing a single solute with molality m is given by [*Lewis and Randall*, 1961]

$$a_w = \exp\left(-\phi \nu M_w m\right), \tag{3}$$

where M_w is the molar mass of water, ν the number of ions into which it is assumed that each molecule of solute dissociates upon dissolution, and ϕ the practical osmotic coefficient, which depends on the solute and its concentration; departures of ϕ from unity result from nonideality and/or incomplete dissociation. The molality can be expressed in terms of ξ, the density of the solution ρ, and the apparent molal volume of the solute V_ϕ (which also depends on solute type and concentration), the latter quantity being defined as the difference, per mole of solute, between the volume of the solution and the volume of the water (calculated as the mass of water divided by the density of pure water ρ_w):

$$V_\phi = \frac{1}{m}\left[\frac{1+mM_s}{\rho} - \frac{1}{\rho_w}\right], \tag{4a}$$

where M_s is the molar mass of the solute. This equation can be rearranged to yield

$$\frac{1+mM_s}{mM_s} = \frac{\rho V_\phi}{M_s} + \frac{1}{mM_s}\frac{\rho}{\rho_w}; \tag{4b}$$

where the left-hand side of this equation, the ratio of the mass of the solution drop to the solute mass, can be also expressed as

$$\frac{1+mM_{\mathrm{s}}}{mM_{\mathrm{s}}}=\frac{\rho r^3}{\rho_{\mathrm{dry}}r_{\mathrm{dry}}{}^3}\equiv\frac{\rho}{\rho_{\mathrm{dry}}}\xi^3\,. \tag{5}$$

Equating (4b) and (5) and solving for m yields

$$m=\frac{\left(\dfrac{1}{M_{\mathrm{s}}}\dfrac{\rho_{\mathrm{dry}}}{\rho_{\mathrm{w}}}\right)}{\xi^3-\dfrac{\rho_{\mathrm{dry}}V_\phi}{M_{\mathrm{s}}}} \tag{6}$$

(and demonstrates that solute concentration can be parameterized by ξ).

Substitution of Eqs. (3) and (6) into Eq. (1) and taking the logarithm of both sides yields

$$\ln h=\frac{\xi_\sigma}{\xi}-\frac{c^3\phi}{\xi^3-\dfrac{\rho_{\mathrm{dry}}V_\phi}{M_{\mathrm{s}}}}, \tag{7}$$

where the constant $c\equiv[\nu(M_{\mathrm{w}}/M_{\mathrm{s}})(\rho_{\mathrm{dry}}/\rho_{\mathrm{w}})]^{1/3}$ is near unity for most substances of interest, being equal to 0.90 for ammonium sulfate (ν=3) and 1.10 for sodium chloride (ν=2), and intermediate to these two values for many inorganic solutes: 0.94 for ammonium bisulfate (ν=3), 0.93 for letovicite [$(NH_4)_3H(SO_4)_2$] (ν=6), 0.92 for ammonium nitrate (ν=2), 1.01 for ammonium chloride (ν=2), 1.01 for sodium sulfate (ν=3), 1.03 for sodium bisulfate (ν=3), and 0.99 for sodium nitrate (ν=2). Equation (7) is exact, so long as the dependences of ξ_σ, ϕ, and V_ϕ on solute concentration are taken into account.

To arrive at what is typically called the Köhler equation several approximations are made, each based on the assumption that the solute concentration is low and thus that ξ is large and h is near unity. First, the quantity ln h is approximated as -(1-h). Next, the values of $\bar{v}_{\mathrm{w}}$ and σ are taken as their values for pure water, with the result that ξ_σ is replaced by $\xi_{\sigma,0}$ (such an approximation is expected to be accurate for inorganic solutes, although it might not be for surface-active substances, which even in very low concentrations can drastically reduce the surface tension of the solution-air interface). Next, the quantity $\rho_{\mathrm{dry}} V_\phi / M_{\mathrm{s}}$ is omitted as being negligible compared to ξ^3, the ratio of these quantities being the one minus the fraction of the volume of the solution occupied by the water, calculated as the mass of the water divided by the density of pure water (as the volume of the solution is not necessarily equal to the sum of the volumes of the water and of the solute, calculated as their masses divided by their respective densities, the ratio of $\rho_{\mathrm{dry}} V_\phi / M_{\mathrm{s}}$ to ξ^3 is not necessarily the same as the volume fraction of the solution occupied by the solute). Finally, ϕ is taken as unity, its limiting value for infinitely dilute solutions. This approximation, together with the assumption that ln h can be accurately approximated by -(1-h), implies that the decrease in the water activity due to the presence of the solute (i.e., the vapor-pressure lowering) is equal to number of moles of ions per mole of water.

With these approximations Eq. (7) can be written as

$$-(1-h) = \frac{\xi_{\sigma,0}}{\xi} - \frac{c^3}{\xi^3}, \tag{8}$$

often termed the Köhler equation, solution of which yields the equilibrium radius ratio ξ solely in terms of h and the dimensionless constants $\xi_{\sigma,0}$ and c, of which only $\xi_{\sigma,0}$ depends on r_{dry} and only c depends on the solute. The first term on the right hand side of this equation, which contains the dependence on surface tension, is denoted the Kelvin term and the second term the Raoult term, their ratio quantifying the importance of the Kelvin effect to the equilibrium relative humidity.

Although it is difficult to draw general conclusions on the accuracy of the Köhler model over a wide range of drop size, solute type, and fractional relative humidity, results are presented below for three situations, each of different relative importance of the Kelvin term to the Raoult term: when the Kelvin effect is of negligible importance (i.e., bulk solution drops); $h = 1$; and activation, which occurs when h attains the maximum value for which equilibration can occur. For situations in which the Kelvin effect can be neglected, ξ can be determined from Eq. (8) as

$$\xi = \frac{c}{(1-h)^{1/3}} . \tag{9}$$

As h approaches unity, the Kelvin term becomes increasingly important, and for h equal to unity, when the Kelvin term and Raoult term are equal in magnitude, the radius ratio ξ_1 can be obtained from Eq. (8) as

$$\xi_1 = \left(\frac{c^3}{\xi_{\sigma,0}} \right)^{1/2} , \tag{10}$$

and the radius r_1 is given by

$$r_1 = \left(\frac{c^3 r_{\text{dry}}{}^3}{r_{\sigma,0}} \right)^{1/2} . \tag{11}$$

As h increases above unity the drop becomes supersaturated with respect to water vapor (with supersaturation $s \equiv h\text{-}1$), and ξ increases until at a value of h, denoted h_{act}, the drop is said to activate; for larger values of h equilibrium is not possible, and the drop continues to grow without bound. At activation the magnitude of the Kelvin term is three times that of the Raoult term, and according to Eq. (8) the radius ratio ξ_{act} is given by

$$\xi_{\mathrm{act}} = \left(\frac{3c^3}{\xi_{\sigma,0}} \right)^{1/2} = 3^{1/2} \xi_1 , \tag{12}$$

and the radius r_{act} by

$$r_{\mathrm{act}} = \left(\frac{3c^3 r_{\mathrm{dry}}{}^3}{r_{\sigma,0}} \right)^{1/2} = 3^{1/2} r_1 . \tag{13a}$$

The supersaturation at activation, also known as the critical supersaturation, is obtained from Eq. (8) as

$$s_{\mathrm{act}} = 2\left(\frac{\xi_{\sigma,0}}{3c} \right)^{3/2} \equiv 2\left(\frac{r_{\sigma,0}}{3c r_{\mathrm{dry}}} \right)^{3/2} = \frac{2}{3} \frac{r_{\sigma,0}}{r_{\mathrm{act}}} . \tag{14a}$$

Thus, on a log-log plot, graphs of r_1 vs. r_{dry} and r_{act} vs. r_{dry} are straight lines with slope 3/2, and a graph of s_{act} vs. r_{dry} is a straight line with slope -3/2; these are shown for solution drops of ammonium sulfate and sodium chloride in Figs. 2, 3, and 4, respectively.

Equations (13a) and (14a) can also be written in a form that readily allows calculation as

$$r_{\mathrm{act}} = r_{\mathrm{dry}} \left(\frac{r_{\mathrm{dry}}}{\breve{r}} \right)^{1/2} , \tag{13b}$$

where $\breve{r} = r_{\sigma,0}/(3c^3)$ is approximately equal to 0.51 nm for ammonium sulfate and 0.27 nm for sodium chloride, and

$$s_{\mathrm{act}} = \left(\frac{\hat{r}}{r_{\mathrm{dry}}} \right)^{3/2} , \tag{14b}$$

where $\hat{r} = 2^{2/3} r_{\sigma,0}/(3c)$ is approximately equal to 0.65 nm for ammonium sulfate and 0.53 nm for sodium chloride. Additionally, Eq. (14a) can be inverted to yield $r_{\mathrm{dry,c}}$, the value of the dry radius of the smallest particle that will activate at given supersaturation:

$$r_{\mathrm{dry,c}} = \frac{r_{\sigma,0}}{3c}\left(\frac{2}{s}\right)^{2/3} \approx \frac{0.58\,\mathrm{nm}}{c \cdot s^{2/3}}. \tag{15}$$

Thus, for example, at (0.1, 0.5, 1.0)% supersaturation, for which s = (0.001, 0.005, 0.01), activation will occur for ammonium sulfate drops with r_{dry} > (65, 22, 14) nm and sodium chloride drops with r_{dry} > (53, 18, 11) nm.

2.2 Solution and approximate solutions to the Köhler equation for $h < 1$

For h less than unity, Eq. (8) can be expressed in an alternative form though introduction of the scaled radius ratio $z = (\xi/c)(1-h)^{1/3}$ and the scaled Kelvin factor $\varepsilon = (\xi_{\sigma,0}/c)/(1-h)^{2/3}$ as

$$z^3 + \varepsilon z^2 - 1 = 0, \tag{16}$$

where the second term in the equation is the Kelvin term and the third term is the Raoult term (similar analysis could also be applied to the situation $h \geq 1$, thus including situations pertinent to cloud drop activation). The quantity ε, which is an increasing function of h and increases without bound as h approaches unity from below, characterizes the importance of the Kelvin effect; for $\varepsilon \ll 1$ this effect is unimportant, but as ε approaches unity this effect becomes increasingly important.

Although not apparent in Eq. (8), for which ξ depends upon the three quantities h, $\xi_{\sigma,0}$ and c, the solution to Eq. (16) depends only upon ε. As this equation is a cubic, it can be solved analytically for $z(\varepsilon)$, from which ξ can be obtained as an explicit function of h

for given r_{dry}. For any positive ε greater than its minimum value $\xi_{\sigma,0}/c$ (equivalently, for any h such that $0<h<1$) there is one real positive solution given by

$$z = \frac{-\varepsilon}{3} + \left[\left(\frac{1}{2} - \frac{\varepsilon^3}{27}\right) + \left(\frac{1}{4} - \frac{\varepsilon^3}{27}\right)^{1/2}\right]^{1/3} + \left[\left(\frac{1}{2} - \frac{\varepsilon^3}{27}\right) - \left(\frac{1}{4} - \frac{\varepsilon^3}{27}\right)^{1/2}\right]^{1/3}, \qquad (17)$$

shown in Fig. 5. However, this expression, although exact, provides little insight into the functional dependence of z upon ε (or of ξ upon h and r_{dry}), and approximate solutions prove easier to use and can be extended to situations in which the basic assumption made in the derivation of the Köhler equation (i.e., low solute concentration) is not satisfied.

Solutions to Eq. (16) can readily be obtained for the limits $\varepsilon << 1$ (when the Kelvin effect is unimportant) and $\varepsilon >> 1$ (h very near unity). In the first limit $z = 1$, which is equivalent to Eq. (9), ξ being a power law in (1-h) with exponent -1/3, and in the second limit $z = \varepsilon^{-1/2}$, which yields the value given by Eq. (10) for ξ_1; solutions for both of these limits are also shown in Fig. 5. The lowest-order correction to the solution of Eq. (16) in the limit $\varepsilon << 1$ can be obtained by assuming $z = z_0 + \varepsilon z_1 + \ldots$, where $z_0 = 1$ and each successive term contains a higher power of ε. This procedure results in $z_1 = -1/3$ and thus $z \approx 1 - \varepsilon/3$, or equivalently,

$$\xi \approx \frac{c}{(1-h)^{1/3}} - \frac{\left(r_{\sigma,0}/r_{\text{dry}}\right)}{3(1-h)}, \qquad (18)$$

consistent with the lowest-order Kelvin correction to the radius ratio [*Lewis*, 2006] for a power law of the form given by Eq. (9) for h near unity; cf. Eq. (2). This expression for z, shown in Fig. 5, agrees with the exact solution to within a few percent for $\varepsilon <$ ~0.5, but the agreement rapidly diminishes with further increase in ε. This procedure could be continued to yield higher-order corrections, but such an attempt would be of little value because of the approximations that were made to obtain the Köhler equation.

Approximate solutions can be found that apply over the entire range of positive ε (h<1) and that have the correct limit for large ε and the correct limit and lowest-order correction for small ε, but good accuracy can be obtained by simpler expressions, such as $z = (1+\varepsilon^{n/2})^{-1/n}$ for $n > 0$. This expression, which yields the correct limits for both $\varepsilon << 1$ and $\varepsilon >> 1$, can be quite accurate: for $n = 2.5$ it agrees with the exact solution to within 1.5%, and for $n = 3$ (shown in Fig. 5) to within 6%, for all positive ε. The approximate solution for $n = 3$, $z = (1+\varepsilon^{3/2})^{-1/3}$, is used here because of its accuracy and simplicity, and because it can readily be extended to situations for which the basic assumption used to derive the Köhler equation is not satisfied, as is done below. Although this expression does not provide the correct functional dependence on r_{dry} of the lowest-order correction given by Eq. (18), this is not of great consequence, as this correction is relatively unimportant in situations for which it is sufficiently small that higher-order corrections are not required. In terms of the radius ratio this expression can be written as

$$\xi = \frac{c}{\left[1 - h + \left(\frac{\xi_{\sigma,0}}{c}\right)^{3/2}\right]^{1/3}} \equiv \frac{c}{\left(1 - h + \frac{\xi_{\sigma,0}}{\xi_1}\right)^{1/3}}, \qquad (19)$$

where ξ_1 is the value of the radius ratio at $h = 1$ given by Eq. (10) for the Köhler model.

The expression for ξ given by Eq. (19) satisfies the equation

$$-(1-h) = \frac{\xi_{\sigma,0}}{\xi}\left[\frac{\xi}{\xi_1}\right] - \frac{c^3}{\xi^3}, \qquad (20)$$

which differs from Eq. (8) only by the factor $[\xi/\xi_1]$ in the Kelvin term. This factor, equal to $z\varepsilon^{1/2}$, is less than unity for $h < 1$, but as the Kelvin term is important only when ξ is nearly equal to ξ_1 (when the factor is nearly equal to unity), the consequences of the approximation that this factor is unity are slight (Fig. 5). In essence, Eq. (19) follows from the assumption that the Kelvin term evaluated at ξ_1 applies to all situations. As $\xi < \xi_1$ for $h < 1$, evaluation of the surface tension term at ξ_1 results in an underestimation of the Kelvin correction and thus an overestimation of the radius (and radius ratio) in this range of relative humidity (and an underestimation for h>1). The result of this assumption is that the expression for ξ in terms of h is the same as that given by Eq. (9) for which the Kelvin effect is neglected, but with h decreased by $\xi_{\sigma,0}/\xi_1$, which is equal to the Kelvin correction at h=1; for c = 1, this decrease is approximately equal to (0.04, 0.01, 0.003, 0.001) for r_{dry}=(10, 25, 50, 100) nm. A graph of ξ vs. h according to Eq. (19) is obtained from that for which the Kelvin correction is neglected by shifting the curve to the right by a constant amount $\xi_{\sigma,0}/\xi_1$; as the graph of ξ vs. h is fairly flat for h appreciably less than unity (when the Kelvin effect can be neglected), such a horizontal shift, even though much greater than that due to the Kelvin effect at these values of h, results in very little error.

2.3 Critical examination of the Köhler equation

Quantification of the approximations made in the derivation of the Köhler equation, Eq. (8), from the exact expression, Eq. (7), allows determination of the range of conditions for which the Köhler equation can be expected to yield accurate results and identification of which approximation limits extension of the model to more concentrated solutions and to values of h farther from unity. This process is achieved by rewriting Eq. (7) as

$$-(1-h)\left[\frac{\ln h}{-(1-h)}\right]=\frac{\xi_{\sigma,0}}{\xi}\left[\frac{\xi_{\sigma}}{\xi_{\sigma,0}}\right]-\frac{c^3}{\xi^3}\left[\phi\left(1-\frac{\rho_{\mathrm{dry}}V_{\phi}}{M_{\mathrm{s}}\xi^3}\right)^{-1}\right], \tag{21}$$

where the factor in brackets on the left-hand side of the equation is denoted F_h, the factor in brackets in the Kelvin term is denoted F_{K}, and that in the Raoult term F_{R}, which can be written as the product of two factors, $F_{\phi} \equiv \phi$ and

$$F_{\xi} \equiv \left(1-\frac{\rho_{\mathrm{dry}}V_{\phi}}{M_{\mathrm{s}}\xi^3}\right)^{-1}. \tag{22}$$

Although F_h depends on h, the other factors depend only on solute concentration (for given solute and temperature), which can be parameterized in terms of the water activity a_{w}. Equation (21) is exact; the Köhler equation follows from the assumption that each of the factors F_h, F_{K}, and F_{R} is equal to unity. However, it is not the individual factors F_h, F_{K}, and F_{R} that determine the accuracy of results obtained using the Köhler model, but the differences of the ratios F_{R}/F_h and F_{K}/F_h from unity, where in computing these ratios for a given solute the value of a_{w} corresponding to a given h, which depends on the value of r_{dry} according to Eq. (1), must be used. Of course the relative importance of the terms themselves must be considered; for instance, in situations for which the Kelvin effect is negligible the factor F_{K}, and thus the ratio F_{K}/F_h, has virtually no effect on the equilibrium radius ratio.

These factors are displayed in Fig. 6 for solution drops of ammonium sulfate and sodium chloride (values of $F_K \equiv r_{\sigma}/r_{\sigma,0}$ in the range of a_{w} corresponding to solutions that are supersaturated with respect to the solute are determined as for Fig. 1). Each of the several factors is equal to unity for a_w (or h, in the case of F_h) equal to unity, but whereas with decreasing a_w (or h) both F_K and F_h initially slowly increase (and continue to increase monotonically), F_R initially decreases extremely rapidly (this behavior typically holds for most inorganic solutes, although for organic solutes the surface tension, and thus F_K, might initially decrease rapidly with decreasing a_w). As F_ξ increases monotonically with decreasing a_w, the initial decrease in F_R is due to F_ϕ (i.e., ϕ). This decrease results from the electrolytic nature of the solution [*Debye and Hückel*, 1923; *Debye*, 1924] and is quite rapid: as a_w decreases from unity to 0.995 (corresponding to molality 0.12 mol kg^{-1} for ammonium sulfate solutions and 0.15 mol kg^{-1} for sodium chloride solutions), ϕ decreases from unity to 0.77 and 0.93, respectively, for these substances. With continued decrease in a_w, ϕ continues to decrease for both substances until reaching a minimum near 0.62 at $a_w \approx 0.94$ for ammonium sulfate solutions and near 0.92 at $a_w \approx 0.99$ for sodium chloride solutions, although with further decrease in a_w the behavior of ϕ differs between these two substances: at $a_w = 0.80$, ϕ is near 0.70 for ammonium sulfate solutions and near 1.21 for sodium chloride solutions. The dependence of ϕ on solute concentration thus depends strongly on the solute.

Numerous formulations for this dependence have been presented—that of *Pitzer* [1973] probably being the best known—but although based in theory these are to large extent empirical, typically containing several terms in powers of molality or some other measure of concentration. The extremely rapid initial decrease in ϕ from unity and further nonuniform behavior with increasing concentration precludes realization of a simple parameterization for this quantity, complicating attempts to find a parameterization for ξ as a function of h and r_{dry} that is accurate over a wide range of h up to very near unity.

The assumption that the practical osmotic coefficient ϕ is equal to unity (i.e., F_ϕ=1) is clearly the limiting one with regard to the accuracy of the Köhler model (Fig. 6), and as this assumption is approximately satisfied only for an extremely narrow range of water activities near unity, it thus restricts the conditions for which this model can be accurately applied to extremely dilute solutions. For example, for ammonium sulfate solution drops with $a_w > 0.95$ the factors F_K and F_ξ are greater than unity by less than 4% and 10%, respectively, whereas F_ϕ is less than unity by up to nearly 40%. For sodium chloride solution drops over this range of a_w the corresponding factors F_K and F_ξ are greater than unity by less than 3%, whereas F_ϕ is less than unity by up to 8%. Thus in many situations inaccuracies resulting from the Köhler model can be estimated to good approximation as being due only to the difference of ϕ from unity, and the range of situations for which the model can yield accurate results could be extended through consideration of a modified Köhler equation of the form

$$-(1-h) = \frac{\xi_{\sigma,0}}{\xi} - \frac{c^3\phi}{\xi^3}, \tag{23}$$

which differs from Eq. (8) only in the factor ϕ in the last term.

Other investigators have noted that the primary quantity determining the relationship between h and ξ for drops at high relative humidity is $c^3\phi$, which is often termed B and referred to as the particle composition parameter [*Fitzgerald et al.*, 1982], the hygroscopicity parameter [*Hudson and Da*, 1996], or the hygroscopicity [*Ghan et al.*, 2001]; the hygroscopicity parameter κ of *Petters and Kreidenweis* [2007], equal to $[c^3/(\nu m M_w)]\{\exp[\phi(\nu m M_w)]-1\}$ for a single solute, is also equal to $c^3\phi$ for low concentrations. However, none of these quantities is a constant because of the dependence of ϕ on solute concentration (and hence on ξ), thus limiting their use in characterizing the hygroscopicity of a given solute (additionally, any such characterization is based on the assumption that ξ_σ is nearly independent of composition and can be accurately approximated by $\xi_{\sigma,0}$, but although this may be true for inorganic solutes, for which small concentrations do not appreciably change the surface tension, even small amounts of surface-active organic substances can drastically reduce the surface tension and thus ξ_σ). Because of the strong dependence of ϕ upon ξ, Eq. (23) is of limited value, as it is not easily amenable to analytic investigation and cannot be inverted to yield a simple expression of the form $\xi = \xi(h, \xi_\sigma)$. However, for extremely dilute solutions, for which the rapid decrease in ϕ from unity with increasing concentration can be accurately parameterized in terms of ξ (the Debye limit), it is possible to obtain estimates for the errors in the Köhler model; these are derived in Appendix A and are presented below.

2.4 Inaccuracies resulting from the Köhler model

In this section the consequences of the approximation that the several F factors are equal to unity are examined and errors resulting from this approximation are quantified for the three situations considered throughout this paper: bulk solution drops, $h = 1$, and activation. The fractional error in the equilibrium radius ratio, $\Delta\xi/\xi$, where $\Delta\xi$ is the radius ratio calculated according to the Köhler model minus the actual value, is presented, as are the fractional errors in the critical value of the supersaturation for given r_{dry}, and in the critical value of the dry radius for given s, for the Debye limit obtained in Appendix A.

For bulk solution drops the equilibrium radius ratio can be obtained from Eq. (21) as

$$\xi = \frac{c}{(1-h)^{1/3}} \left(\frac{F_\mathrm{R}}{F_h} \right)^{1/3}, \tag{24}$$

with corresponding fractional error given by

$$\frac{\Delta \xi}{\xi} = \left(\frac{F_h}{F_\mathrm{R}} \right)^{1/3} - 1, \tag{25}$$

where F_R is evaluated at $a_\mathrm{w} = h$. As the ratio $F_\mathrm{h}/F_\mathrm{R}$ varies from 0.74 to 1.51 for ammonium sulfate and from 0.70 to 1.09 for sodium chloride over the respective ranges of h for which solution drops exist, the fractional error in ξ varies from -10% to +15% for ammonium sulfate and from -11% to +3% for sodium chloride. Even over the range $0.90 < h < 0.99$ the fractional error in ξ exceeds 10% for ammonium sulfate solution drops, primarily because of the decrease of ϕ to near 0.7 within this range.

For $h = 1$ the equilibrium radius ratio ξ_1 can be obtained from Eq. (21) as

$$\xi_1 = \left(\frac{c^3}{\xi_{\sigma,0}} \right)^{1/2} \left(\frac{F_\mathrm{R}}{F_\mathrm{K}} \right)^{1/2}, \tag{26}$$

with fractional error given by

$$\frac{\Delta \xi_1}{\xi_1} = \left(\frac{F_\mathrm{K}}{F_\mathrm{R}} \right)^{1/2} - 1 \tag{27}$$

(Fig. 2), where both F_R and F_K are evaluated at the water activity corresponding to $h = 1$ for the given r_dry according to Eq. (1). As when $h = 1$ the water activity is near unity for r_dry greater than ~20 nm (Fig. 1), F_K is very near unity and the difference of F_R from unity is due mainly to the practical osmotic coefficient at $h = 1$, ϕ_1, shown as a function of r_{dry} in Fig. 7 for ammonium sulfate and sodium chloride solution drops. Thus for drops in this size range Eq. (27) can be accurately approximated as

$$\frac{\Delta\xi_1}{\xi_1} \approx \frac{1}{\phi_1^{1/2}} - 1\,, \tag{28}$$

with the approximation becoming more accurate with increasing r_{dry}. In the Debye limit this quantity (Appendix A) is given by

$$\frac{\Delta\xi_1}{\xi_1} = \left(\frac{\tilde{r}_1}{r_{\text{dry}}}\right)^{3/4} \tag{29}$$

(also shown in Fig. 2), where $\tilde{r}_1 \approx$ 5.0 nm for ammonium sulfate solutions and 1.0 nm for sodium chloride solutions.

As activation occurs when h takes its maximum value for which equilibrium is possible, expressions for ξ_{act}, s_{act}, and $r_{\text{dry,c}}$, and for the fractional errors in these quantities, can be determined by differentiation of Eq. (21) with respect to ξ (the fractional error in ξ_{act} is shown in Fig. 3, and s_{act} and its fractional error in Fig. 4). However, these expressions, which involve F_{R}, F_{K}, and their derivatives with respect to ξ, are cumbersome and must be evaluated at the water activity corresponding to activation, which must be determined iteratively. Because a_{w} is very near unity at activation for a wide range of drop sizes, most of the inaccuracies in ξ_{act}, s_{act}, and $r_{\text{dry,c}}$ are due solely to the assumption that ϕ_{act} (shown in Fig. 8 as a function of r_{dry} for solution drops of ammonium sulfate and sodium chloride) is equal to unity. For example, activation occurs at supersaturations less than 2% (i.e., $h_{\text{act}}<1.02$) for solution drops of these substances with $r_{\text{dry}} > 10$ nm, thus F_h is greater than unity by less than 1%, and F_{K} and F_ξ by less than 1% and 2% for ammonium sulfate, and less than 0.5% and 0.3% for sodium chloride, whereas ϕ_{act} takes values as low as 0.71 for ammonium sulfate and 0.93 for sodium chloride (Fig. 8). Hence in considering activation the factors F_h, F_{K}, and F_ξ can be taken as unity (as noted above, this might not be true for drops containing surface-active substances, for which F_{K} could be considerably less than unity even for low concentrations), and F_{R} can be taken as equal to F_ϕ, with little loss in accuracy. Such a procedure, equivalent to considering Eq. (23) as exact, allows ξ_{act}, s_{act}, and $r_{\mathrm{dry,c}}$ and their fractional errors to be expressed in terms of only ϕ and its derivative at activation (Appendix A).

In the Debye limit the fractional errors take an especially simple form that clearly illustrates their dependences on r_{dry} (Appendix A). That in ξ_{act} is given by

$$\frac{\Delta\xi_{\mathrm{act}}}{\xi_{\mathrm{act}}} = \left(\frac{\tilde{r}_{\mathrm{act}}}{r_{\mathrm{dry}}}\right)^{3/4} \tag{30}$$

(Fig. 3), where $\tilde{r}_{\mathrm{act}} \approx 2.8$ nm for ammonium sulfate solutions and 0.58 nm for sodium chloride solutions, and that in s_{act} (Fig. 4) is opposite in sign and two-thirds the magnitude of that in ξ_{act}. Similarly, the fractional error in $r_{\mathrm{dry,c}}$ for given supersaturation is given by

$$\frac{\Delta r_{\mathrm{dry,c}}}{r_{\mathrm{dry,c}}} = -\left(\frac{s}{\tilde{s}}\right)^{1/2}, \tag{31}$$

where $\tilde{s} \approx 4.4$ for sodium chloride and 0.55 for ammonium sulfate; at 1% supersaturation (s=0.01) this corresponds to 5% for a sodium chloride and 14% for ammonium sulfate.

Inaccuracies resulting from the Köhler model decrease with increasing r_{dry} for sufficiently large drops (Figs. 2, 3, 4), but they may still be appreciable, even for solutions as dilute as those at activation. For instance, according to Eqs. (13) and (14), at typical maximum supersaturations in clouds of 0.1-0.5%, ammonium sulfate particles with dry radii of ~20-65 nm activate to form drops with radii ~150-750 nm, but from Fig. 3 it is seen that the Köhler model overestimates these activation radii by 10-20%.

2.5 Extensions of the Köhler model

Attempts have been made to extend the range of validity of the Köhler model to higher concentrations by modification of one or more of the terms in Eq. (8), or equivalently by different choices of F factors. To be useful, such modifications should apply to different solutes and should retain the simplicity of the basic Köhler equation, amenable to analytic investigation, as otherwise there would be no advantage over using Eq. (1) to determine ξ from h for a given r_{dry}. Retention of ln h instead of -(1-h) in Eq. (7), in effect resulting in higher-order terms on the right-hand side of this equation from expansion of an exponential, gains little, as it leads to a more complicated equation and other inaccuracies typically dominate that of F_h.

Most prior approaches have focused on the Raoult term (i.e., the factor F_{R}). It is typically assumed that the reduction in water activity due to the presence of the solute is equal to the moles of ions per mole of water or to the mole fraction of the ions, and that volume additivity of water and solute holds (that is, that the volume of the solution is equal to the sum of the volumes of the water and solute, calculated by their masses divided by their respective densities). While these assumptions seem reasonable and lead to Eq. (8) for low concentrations, different results are obtained when such assumptions are used to extend the treatment to higher concentrations.

The assumption that the reduction in water activity is equal to the ratio of the number of moles of ions to moles of water (a quantity that is directly proportional to the molality), and the assumption that it is equal to the mole fraction of the ions, both yield $\phi = 1$ to lowest-order in m, but to next order the first assumption implies $\phi = 1 + \nu m M_w/2$ and the second one $\phi = 1 - \nu m M_w/2$. As ϕ decreases from unity with increasing concentration initially as $m^{1/2}$ (Appendix A), neither of these assumptions yields the correct dependence of the vapor-pressure lowering on concentration or captures the rapid decrease in ϕ from unity, which is the main source of inaccuracy in results obtained from the Köhler model. Thus extensions of this model to more concentrated solutions based on either of these assumptions cannot be expected to yield accurate results.

The assumption of volume additivity implies that the apparent molal volume of the solute V_ϕ is equal to M_s/ρ_{dry}, and thus that $\rho_{dry}V_\phi/M_s$ is equal to unity, independent of solute concentration (and temperature). Although this assumption may result in small error in calculation of the density, it is typically not satisfied, especially for dilute solutions. For instance, as a_w decreases from very nearly unity to 0.99 to 0.97 at 25ºC, V_ϕ increases from approximately 52 to 56 to 60 $cm^3\ mol^{-1}$ for ammonium sulfate solutions (calculated using the fit given by Albright et al., 1994), corresponding to an increase in $\rho_{dry}V_\phi/M_s$ of 0.70 to 0.75 to 0.80, and from approximately 16.6 to 17.6 to 18.4 $cm^3\ mol^{-1}$ for sodium chloride solutions (calculated using the fit given by Chen et al., 1980), corresponding to an increase in $\rho_{dry}V_\phi/M_s$ of 0.61 to 0.65 to 0.68. Results vary for different substances, and V_ϕ may even be less than zero (as for Na_2CO_3, $MgSO_4$, and $CaCO_3$ at extremely low concentrations at 25ºC), although for most solutes of interest V_ϕ increases with increasing concentration. The assumption of volume additivity implies

$F_\xi = \xi^3/(\xi^3 - 1)$ and results in replacement of the expression $\xi^3 - \rho_{dry}V_\phi/M_s$, which was taken as ξ^3 in the derivation of the Köhler equation, by $\xi^3 - 1$, leading to a quartic equation for ξ. Such an approximation would be more accurate for situations in which the quantity $\rho_{dry}V_\phi/M_s$ were near unity, but overall there is little to be gained by this approach, and whether ξ^3 or $\xi^3 - 1$ is used is of little consequence when the dominant error in the Köhler model is the assumption that ϕ is equal to unity.

3. Parameterization of radius ratio in terms of relative humidity and dry radius

Obtaining a simple expression for the equilibrium radius ratio $\xi = \xi(h, \xi_\sigma)$ that is accurate up to and including $h = 1$ for a wide range of r_{dry} (i.e., ξ_σ) is complicated by two primary factors: the rapid increase in the practical osmotic coefficient toward unity as a_w approaches unity (Fig. 6), and the increase in the importance of the Kelvin effect as h approaches unity. The values of h at which these effects occur depends strongly on the dry radius; for example, as r_{dry} for ammonium sulfate solution drops increases from 20 to 50 to 100 nm, the value of h at which the Kelvin term is 25% of the Raoult term increases from 0.88 to 0.97 to 0.99. For sufficiently small r_{dry}, the range of water activity corresponding to $h < 1$ is sufficiently far from unity (Fig. 1) that ϕ varies smoothly, allowing accurate (but empirical) parameterization; however, for larger drops parameterization becomes difficult because of the interplay of the above factors.

In situations for which the Kelvin effect can be neglected the expression for the radius ratio $\xi = \xi(h, \xi_\sigma)$ should reduce to a function only of h. One such expression which is accurate for h less than ~0.9 is a power law in $(1-h)$ with exponent in the range -0.2 to

-0.3 (the exact value depending on solute), a form first used by *Keith and Arons* [1954] for sea salt aerosol particles and later by *Kasten* [1969] for other aerosol particles. This empirical expression in effect assumes that F_R/F_h can be accurately approximated by a power law in (1-h) with an exponent in the range 0.1-0.4. In some situations the Kelvin effect can be included as an additional perturbation term [*Lewis*, 2006], but for larger values of h and for situations in which the Kelvin effect is too large to treat as a small perturbation another approach must be used.

Any parameterization for the radius ratio containing a dependence on r_{dry} must implicitly include the Kelvin effect [*Lewis*, 2006]. One such parameterization, similar to that proposed by *Fitzgerald* [1975], is

$$\xi = \alpha(h) r_{dry}^{\beta(h)} . \tag{32}$$

Although this expression does not explicitly illustrate the dependence on surface tension, it appears to separate the dependences of ξ on h and r_{dry}, with the dependence of ξ on h for situations in which the Kelvin effect is unimportant described by α (which must have dimension length to the power -β), and with the Kelvin effect being parameterized by β, which must be very near zero except for h very near unity, when it rapidly approaches 1/2 to match the result given by Eq. (10). However, as the value of h for which the Kelvin effect makes a given fractional difference in ξ, and thus at which β begins to rapidly approach 1/2, depends on r_{dry} [*Lewis*, 2006], β must depend on r_{dry} in addition to h. Additionally, α becomes infinite for h = 1 unless it includes a dependence on r_{dry}. As both α and β must depend on both h and r_{dry}, the separation of the dependencies of ξ on h and r_{dry} is not realized and this formulation does not retain the simplicity of the original model. Furthermore, there appears to be no indication of how the functions α and β could be chosen, nor any physical basis for such a choice.

3.1 New formulation for radius ratio valid up to h=1

In this section the above analysis of the Köhler model is used to obtain an expression for ξ as a function of h and ξ_σ valid up to h = 1. Such an expression provides a simple and direct method of calculating the radius of a solution drop with a given mass of known solute without recourse to iterative or recursive methods, and it clearly illustrates the dependences of this radius on fractional relative humidity and dry radius (as well as on surface tension), which is not possible with more complicated models. This expression would also be useful in global models where computational expense is a concern.

For bulk solution drops of many inorganic solutes the equilibrium radius ratio is accurately approximated over a wide range of h by a two-parameter expression of the form

$$\xi = a\left(b + \frac{1}{1-h}\right)^{1/3}, \tag{33}$$

where a and b are chosen empirically to yield a good fit. For h very near unity this expression approaches a power law in (1-h) with exponent -1/3, similar to that given by Eq. (9), although a is not necessarily equal to c. Many previous expressions appear similar [*e.g.*, *Fitzgerald*, 1978; *Gerber*, 1985] but contain only one free parameter, as they assume volume additivity which requires $b = 1/a^3$. Although these expressions provide fairly good fits over a limited range of h, they were formulated for solutions that are undersaturated with respect to the solute and their accuracy is typically not as good for more concentrated solutions (i.e., lower values of h). Additionally, several investigators [*Hänel*, 1968; *Winkler*, 1973; *Zhang et al.*, 1993; *Stein et al.*, 1994; *Fitzgerald et al.*, 1998; *Dick et al.*, 2000; *Brooks et al.*, 2004; *Kreidenweis et al.*, 2005] have proposed expressions similar to Eq. (33) but with the term b replaced by a more complicated function, typically a polynomial in h. However, such expressions, with several adjustable parameters, do not seem necessary to fit the data and their associated uncertainties, and they do not capture the rapid variation in ϕ (and thus the behavior of ξ) at values of h near unity.

The accuracy of Eq. (33) is shown in Fig. 9 for bulk solution drops of ammonium sulfate with parameters $a = 0.78$ and $b = 1.90$, and of sodium chloride with $a = 1.08$ and $b = 1.10$; as noted above, these values were chosen empirically to provide a good fit over a wide range of h. This expression is accurate to within 3% for bulk ammonium sulfate solution drops over the entire range of h from the efflorescence value (~0.40) up to 0.99, and to within 8% for h up to 0.999, but at higher values of h it yields values of ξ that are too low by up to 13%. This error is due almost entirely to the rapid increase in ϕ from 0.72 to 0.86 to unity as h increases from 0.99 to 0.999 to unity (although typically at these values of h the Kelvin effect will be important and must be taken into account). The expression is accurate to within 2% for bulk sodium chloride solution drops for h from the efflorescence value (~0.45) up to unity. In essence, this formulation assumes constant values for the practical osmotic coefficient, $\bar{\phi}$, equal to $(a/c)^3$, and for the apparent molal volume of solute, such that $\rho_{\mathrm{dry}}V_\phi/M_\mathrm{s}$ is equal to a^3b. The above choices for a and b yield 0.65 and 0.95 for $\bar{\phi}$, and 0.90 and 1.4 for $\rho_{\mathrm{dry}}V_\phi/M_\mathrm{s}$, for ammonium sulfate and sodium chloride, respectively. The value of $\bar{\phi}$ for ammonium sulfate is considerably less than unity, but over a wide range of a_w it is near the actual value of ϕ, resulting in a good fit over a wide range of h.

The parameterization given by Eq. (33) can be extended to situations for which the Kelvin effect is important by an approach similar to that used above to obtain Eq. (19), resulting in the expression

$$\xi = a\left[b + \frac{1}{1 - h + \left(\dfrac{\xi_{\sigma,0}}{a}\right)^{3/2}}\right]^{1/3}, \tag{34}$$

which explicitly illustrates the dependences of ξ on h and r_{dry} (contained in $\xi_{\sigma,0}$). This expression implicitly assumes that the Kelvin term evaluated at the radius ratio $\xi = (a^3/\xi_{\sigma,0})^{1/2}$ (which is very nearly equal to radius ratio at $h = 1$ given by this expression) applies for all situations. Thus, similar to the approximate solution to the Köhler equation given by Eq. (19), the radius ratio at a given value of h is that given by Eq. (33) for which the Kelvin effect is neglected, but with h decreased by $(\xi_{\sigma,0}/a)^{3/2}$.

Comparison of the radius ratio obtained from Eq. (34) and that calculated from Eq. (1) is shown in Fig. 9 for solution drops of ammonium sulfate and sodium chloride with r_{dry} = 100, 50, 20, 10, and 5 nm. Overall, the agreement over such a wide range of r_{dry} and h for a quantity which varies by so much is remarkable for an approximation containing only two adjustable parameters, especially considering that much of the inaccuracy results from the approximation for bulk solution drops. For $r_{dry} > 5$ nm Eq. (34) yields estimates of ξ (or r) that are accurate to within ~8% for ammonium sulfate solution drops for $h < 0.999$, and to within 7% for sodium chloride solution drops for h

up to and including unity. For ammonium sulfate solution drops at $h = 1$ it yields values of ξ that are accurate to within a few percent for r_{dry} near 5 nm (because for drops of this size ϕ_1 is near the value chosen for $\bar{\phi}$; Fig. 7), although with increasing r_{dry} the expression becomes less accurate and yields values that are too low by $\bar{\phi}^{1/2}$, or nearly 20%, for large drops due to the increase in ϕ as a_{w} approaches unity. As ϕ_1 for ammonium sulfate solution drops varies from ~0.62 to unity (Fig. 7), the fractional error in ξ_1 according to Eq. (27) varies over a range of ~25% for any constant choice of ϕ. For sodium chloride solution drops at $h = 1$ this parameterization is accurate to within ~3% for $r_{\mathrm{dry}} > 5$ nm.

The largest disagreements occur at relatively high values of h, but at such values uncertainty or variability in h will typically provide larger errors; for instance, for a drop with $r_{\mathrm{dry}} = 50$ nm at $h = 0.97$ an uncertainty of 0.01 in h (which would result from an uncertainty in temperature of ~0.15ºC for fixed water vapor pressure) yields an uncertainty in the radius ratio of more than 10%. Additionally, practical considerations often mitigate this inaccuracy in atmospheric situations because of the extremely long time for large drops to equilibrate at values of h near unity. For example, according to *Lewis and Schwartz* [2004, p. 22], a sea salt aerosol particle with $r_{\mathrm{dry}} = 250$ nm (for which the critical supersaturation is ~0.01%), initially at equilibrium at 80% RH and instantaneously exposed to an environment with supersaturation 0.1% at 0ºC, requires approximately 400 s to attain its activation radius of ~8 μm, and the time required for a sea salt aerosol particle with $r_{\mathrm{dry}} = 500$ nm (for which the critical supersaturation is ~0.003%) to attain its activation radius of ~20 μm under these same conditions is roughly an order of magnitude greater.

3.2 Previous parameterizations

The only previous parameterization for the radius ratio as a function of relative humidity valid up to $h = 1$ is an empirical one proposed by *Gerber* [1985] for four aerosol components: sea salt, "urban", "rural", and ammonium sulfate. This expression can be written in the form

$$\xi = \left(1 + \frac{C_1 r_{\text{dry}}{}^{C_2}}{-\ln h + C_3 r_{\text{dry}}{}^{C_4}} \right)^{1/3} , \tag{35}$$

where the first term in the parentheses (unity) follows from the assumption that the volumes of water and solute are additive; r_{dry} must be given in centimeters for the values of C_i given by Gerber, as some of these constants contain dimensions (the values of C_i here differ slightly from those of Gerber). The dependence of ξ on surface tension (i.e., the Kelvin effect) is not explicitly shown, but is contained in the constants C_i. The quantity C_2 is much less than unity for each of the components considered (taking values 0.079, 0.101, 0.115, 0.082, respectively) and the quantity C_4 is very nearly -1.5 (taking values -1.424, -1.404, -1.399, and -1.428, respectively). If C_2 is taken as zero and C_4 is taken as -1.5, and if the logarithm is expanded about h=1 and only the first term is kept (i.e., if the approximation F_h=1 is made), then Eq. (35) becomes

$$\xi = C_1^{1/3} \left(\frac{1}{C_1} + \frac{1}{1 - h + C_3 \, r_{\text{dry}}{}^{-3/2}} \right)^{1/3} , \tag{36}$$

which has the same functional form as Eq. (34) and is equal to it if $a = C_1^{1/3}$, $b = 1/C_1$, and $C_3 = (r_{\sigma,0}/a)^{3/2}$.

The stated range of validity for this formulation was 10 nm < r_{dry} < 10 μm and the entire range of h up to unity, and the accuracy for $h > 0.75$ was stated as several percent, with a maximum error of more than 13%. However, for $h = 1$ this formulation overestimates the radius ratio of ammonium sulfate solution drops with r_{dry} = 10 nm by more than 15%, and underestimates that for drops with r_{dry} > 1000 nm by approximately 5%. Additionally, the Kelvin effect is overestimated for a wide range of conditions, including drops sufficiently large that it should be negligible. For instance, for ammonium sulfate solution drops at $h = 0.9$, Eq. (35) yields radius ratios of 1.72, 1.81, and 1.91 for r_{dry} = 100, 10^3, and 10^4 nm, respectively, whereas for drops of these sizes the Kelvin effect should reduce the bulk value of $\xi = 1.75$ by ~3 nm/r_{dry}, or 0.03, 0.003, and 0.0003, respectively, according to Eq. (2). The data used by Gerber for ammonium sulfate [*Low*, 1969] extended only up to $a_w = 0.996$, at which $\phi = 0.78$, thus to obtain his fit Gerber evidently extrapolated these data in some manner that did not account for the rapid increase in ϕ toward unity at greater a_w. As the two-parameter expression given by Eq. (34) yields more accurate results for bulk solutions and is presented in dimensionless form, with the Kelvin effect explicitly characterized through the dependence of ξ on r_{dry}, it is preferred to the four-parameter expression given by Eq. (35).

4. Summary

The Köhler model relating the radius ratio ξ of an aqueous solution drop with dry radius r_{dry} to the fractional relative humidity h has been investigated, and the so-called Köhler equation derived in which ξ depends on h and on two dimensionless constants, c

and $\xi_{\sigma,0}$, with only c depending on solute and only $\xi_{\sigma,0}$ depending on particle size. Exact and approximate solutions to this equation are presented for $h < 1$. The assumptions of this model are formulated as approximations that are made in the derivation of the Köhler equation, and these approximations and the resultant inaccuracies are examined and quantified for several situations of interest: when the Kelvin effect can be neglected, at $h = 1$, and at activation. Specific examples are presented for solution drops of ammonium sulfate and sodium chloride. The dominant source of inaccuracy derives from the assumption that the practical osmotic coefficient ϕ is unity, the rapid decrease in this quantity from unity with increasing solute concentration limiting accuracy of the radius or radius ratio determined from this model to up to several tens of percent, depending on the substance. For large drops the errors resulting from this approximation can be accurately estimated using the so-called Debye approximation, which accounts for the initial decrease in ϕ from unity with increasing concentration. Attempts to extend the Köhler model to lower values of h and more concentrated solutions typically do not consider this decrease, and as it provides the dominant contribution to the inaccuracy of this model, these extensions cannot be expected to yield accurate results. Based on analogy with an approximate solution of the Köhler equation, a two-parameter expression for the radius ratio of an aqueous solution drop as a function of h and r_{dry} is presented which yields accurate results for a wide range of r_{dry} (at least down to 5 nm) over the entire range of h up to and including unity.

Acknowledgments

This research was supported by the United States Department of Energy Atmospheric Radiation Measurement Program under contract DE-AC03-98CH10886. The author thanks Stephen E. Schwartz and Jian Wang of Brookhaven National Laboratory and three anonymous referees for helpful comments.

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Appendix A. Approximations in the Debye limit

The practical osmotic coefficient ϕ of an aqueous electrolytic solution depends strongly on the solute and its concentration, precluding simple expressions of general validity. However, for extremely dilute solutions a simple parameterization can be obtained which can be used to yield estimates of the inaccuracy of results of the basic Köhler model. In this so-called Debye limit ϕ decreases from unity with increasing concentration as

$$\phi \approx 1 - A_\phi \left| z_+ z_- \right| I^{1/2} \tag{A.1}$$

[*Debye and Hückel*, 1923; *Debye*, 1924], where A_ϕ is a constant approximately equal to 0.392 $\mathrm{mol}^{1/2}\ \mathrm{kg}^{-1/2}$ at 25ºC, z_+ and z_- are the magnitudes of charges of the positive and negative ions, respectively, into which the electrolyte dissociates in solution, and I is the ionic strength, related to the molality m by $I = m(\nu_+ z_+^2 + \nu_- z_-^2)/2$, where ν_+ and ν_- are the number of the positive and negative ions, respectively, into which a molecule of solute dissociates [*Lewis and Randall*, 1961]. In terms of the molality Eq. (A.1) can be written

$$\phi \approx 1 - A_\phi \left[\left| z_+ z_- \right| \left(\frac{I}{m} \right)^{1/2} \right] m^{1/2} \equiv 1 - A_\phi d m^{1/2}, \tag{A.2}$$

where the factor in brackets, d, depends only on the type of electrolyte; $d = 1$ for 1-1 electrolytes (for which $z_+ = z_- = 1$ and $I = m$), and $d = 2\sqrt{3} \approx 3.5$ for 1-2 and 2-1 electrolytes (for which $I = 3m$). The range of concentrations for which this approximation holds to given accuracy differs for different solutes, but in general it is restricted to quite low concentrations, for which a_w is extremely near unity. For instance, Eq. (A.2) yields $\phi = 0.81$ instead of the actual 0.87 for ammonium sulfate solutions at molality

0.02 mol kg^{-1} (corresponding to $a_w = 0.999$), and $\phi = 0.92$ instead of the actual 0.95 for sodium chloride solutions at molality near 0.05 mol kg^{-1} (corresponding to $a_w = 0.998$).

For very dilute solutions the molality m, given by Eq. (6), can be approximated by

$$m \approx \left(\frac{1}{M_s} \frac{\rho_{dry}}{\rho_w} \right) \left(\frac{1}{\xi^3} \right), \tag{A.3}$$

which differs from the exact value by the factor F_ξ given by Eq. (22); for $a_w > 0.99$ this factor differs from unity by less than 1% for both ammonium sulfate and sodium chloride solutions (as it is the quantity $m^{1/2}$ that is of interest and that determines the difference of ϕ from unity, the inaccuracy resulting from this approximation over this range of a_w is negligible). Substitution of Eq. (A.3) into Eq. (A.2) yields

$$\phi \approx 1 - \left(\frac{K}{\xi} \right)^{3/2}, \tag{A.4}$$

with

$$K = \left(\frac{A_\phi{}^2}{M_w} \right)^{1/3} \left[c \left(\frac{d^2}{\nu} \right)^{1/3} \right], \tag{A.5}$$

where $c \equiv [\nu(M_w/M_s)(\rho_{dry}/\rho_w)]^{1/3}$ as above, and only the quantity in brackets depends on the solute. At 25ºC, K is equal to 1.6c for 1-1 electrolytes, and twice this for 1-2 and 2-1 electrolytes; thus K is equal to 2.9 for ammonium sulfate and 1.8 for sodium chloride (for ammonium nitrate and sodium nitrate, both 1-1 electrolytes, K is equal to 1.5 and 1.6, respectively, and for ammonium bisulfate and for sodium sulfate, both 2-1 electrolytes, it is equal to 3.0 and 3.3, respectively). The approximation given by Eq. (A.4) can be used along with the value of ξ evaluated for the situation under consideration (here either $h = 1$

or activation) to determine the fractional error in the radius ratio obtained from the Köhler model as a function of the dry radius.

For $h = 1$, substitution into Eq. (A.4) of the value ξ_1 given by Eq. (10), which was calculated under the assumption that ϕ is unity, yields the approximation

$$\phi_1 \approx 1 - \left(\frac{K^2 \xi_{\sigma,0}}{c^3} \right)^{3/4} \equiv 1 - \left(\frac{K^2 r_{\sigma,0}}{c^3 r_{\mathrm{dry}}} \right)^{3/4}, \tag{A.6}$$

shown in Fig. 7 along with the exact value of ϕ_1 for ammonium sulfate and sodium chloride solutions as a function of r_{dry}. Substitution of this expression into Eq. (28) yields Eq. (29):

$$\frac{\Delta\xi_1}{\xi_1} \approx \left(\frac{1}{\phi_1^{1/2}} - 1 \right) \approx \frac{1}{2} \left(\frac{K^2 \xi_{\sigma,0}}{c^3} \right)^{3/4} = \left(\frac{\tilde{r}_1}{r_{\mathrm{dry}}} \right)^{3/4}, \tag{A.7}$$

where

$$\tilde{r}_1 = \left(\frac{K^2 r_{\sigma,0}}{2^{4/3} c^3} \right) = \left(\frac{K}{c} \right)^2 \left(\frac{1}{c} \right) \left(\frac{r_{\sigma,0}}{2^{4/3}} \right) \tag{A.8}$$

is equal to 1.1 nm/c for 1-1 electrolytes (and hence 1.0 nm for sodium chloride solutions) and 4.5 nm/c for 1-2 and 2-1 electrolytes (and hence 5.0 nm for ammonium sulfate solutions). The approximation given by Eq. (A.7), together with the fractional error in the radius ratio for the Köhler model, is shown in Fig. 2.

This analysis can be applied also to activation, although that situation is more complicated. Under the assumption that the only contribution to inaccuracy in the Köhler model derives from ϕ, the radius ratio at activation can be obtained from Eq. (23) as

$$\xi_{\mathrm{act}} \approx \left(\frac{3c^3}{\xi_{\sigma,0}} \right)^{1/2} \phi_{\mathrm{act}}^{1/2} \left[1 - \frac{1}{3} \left(\left. \frac{d \ln \phi}{d \ln \xi} \right|_{\mathrm{act}} \right) \right]^{1/2}, \tag{A.9}$$

with fractional error

$$\frac{\Delta\xi_{\text{act}}}{\xi_{\text{act}}} \approx \frac{1}{\phi_{\text{act}}{}^{1/2}\left[1-\frac{1}{3}\left(\left.\frac{d\ln\phi}{d\ln\xi}\right|_{\text{act}}\right)\right]^{1/2}} - 1. \tag{A.10}$$

Substitution into Eq. (A.4) of the value of ξ_{act} from Eq. (12), which was likewise calculated under the assumption that ϕ is equal to unity, yields

$$\phi_{\text{act}} \approx 1-\left(\frac{K^2\xi_{\sigma,0}}{3c^3}\right)^{3/4} \equiv 1-\left(\frac{K^2 r_{\sigma,0}}{3c^3 r_{\text{dry}}}\right)^{3/4}, \tag{A.11}$$

shown in Fig. 8, and

$$1-\frac{1}{3}\left(\left.\frac{d\ln\phi}{d\ln\xi}\right|_{\text{act}}\right) \equiv 1-\frac{1}{3}\frac{\xi}{\phi}\left.\frac{d\phi}{d\xi}\right|_{\text{act}} \approx 1-\frac{1}{2}\left(\frac{K}{\xi_{\text{act}}}\right)^{3/2}. \tag{A.12}$$

Substitution into Eq. (A.10) of these results yields

$$\frac{\Delta\xi_{\text{act}}}{\xi_{\text{act}}} \approx \frac{1}{\left[1-\left(\frac{K}{\xi_{\text{act}}}\right)^{3/2}\right]^{1/2}\left[1-\frac{1}{2}\left(\frac{K}{\xi_{\text{act}}}\right)^{3/2}\right]^{1/2}} - 1 \approx \frac{3}{4}\left(\frac{K}{\xi_{\text{act}}}\right)^{3/2}, \tag{A.13}$$

which can be simplified to yield Eq. (30):

$$\frac{\Delta\xi_{\text{act}}}{\xi_{\text{act}}} \approx \frac{3}{4}\left(\frac{K}{\xi_{\text{act}}}\right)^{3/2} \approx \frac{3}{4}\left(\frac{K^2\xi_{\sigma,0}}{3c^3}\right)^{3/4} = \left(\frac{\tilde{r}_{\text{act}}}{r_{\text{dry}}}\right)^{3/4}, \tag{A.14}$$

where

$$\tilde{r}_{\text{act}} = \left(\frac{3^{1/3}K^2 r_{\sigma,0}}{2^{8/3}c^3}\right) = \left(\frac{K}{c}\right)^2\left(\frac{1}{c}\right)\left(\frac{3^{1/3}r_{\sigma,0}}{2^{8/3}}\right) = \left(\frac{3}{16}\right)^{1/3}\tilde{r}_1 \approx \frac{\tilde{r}_1}{1.7} \tag{A.15}$$

is equal to 0.64 nm/c for 1-1 electrolytes (and hence 0.58 nm for sodium chloride solutions) and 2.6 nm/c for 1-2 and 2-1 electrolytes (and hence 2.8 nm for ammonium sulfate solutions). The approximation given by Eq. (A.14), together with the fractional error in the radius ratio for the Köhler model, is shown in Fig. 3. Two-thirds of the fractional error in $\xi_{\rm act}$ derives from $\phi_{\rm act}{}^{1/2}$ and one-third from the term containing the derivative of $\phi_{\rm act}$.

The supersaturation at activation $s_{\rm act}$ can likewise be calculated as

$$s_{\rm act} = 2\left(\frac{\xi_{\sigma,0}}{3c}\right)^{3/2}\left(\frac{1}{\phi_{\rm act}{}^{1/2}}\right)\frac{\left[1-\frac{1}{2}\left(\left.\frac{d\ln\phi}{d\ln\xi}\right|_{\rm act}\right)\right]}{\left[1-\frac{1}{3}\left(\left.\frac{d\ln\phi}{d\ln\xi}\right|_{\rm act}\right)\right]^{3/2}}, \tag{A.16}$$

with the fractional error in this quantity given by

$$\frac{\Delta s_{\rm act}}{s_{\rm act}} \approx \phi_{\rm act}{}^{1/2}\frac{\left[1-\frac{1}{3}\left(\left.\frac{d\ln\phi}{d\ln\xi}\right|_{\rm act}\right)\right]^{3/2}}{\left[1-\frac{1}{2}\left(\left.\frac{d\ln\phi}{d\ln\xi}\right|_{\rm act}\right)\right]}-1, \tag{A.17}$$

which in the Debye limit can be approximated using the same techniques as above by

$$\frac{\Delta s_{\rm act}}{s_{\rm act}} \approx \frac{-1}{2}\left(\frac{K}{\xi_{\rm act}}\right)^{3/2} = \frac{-2}{3}\left(\frac{\tilde{r}_{\rm act}}{r_{\rm dry}}\right)^{3/4}, \tag{A.18}$$

opposite in sign and two-thirds the magnitude of the fractional error in the radius ratio at activation. Both the fractional error in supersaturation resulting from the Köhler model and the approximate value given by Eq. (A.18) are shown in Fig. 4.

Similarly, the critical value of $r_{\rm dry}$ for given supersaturation can be obtained from Eq. (A.16) as

$$r_{\mathrm{dry,c}} = \left(\frac{2}{s}\right)^{2/3} \left(\frac{r_{\sigma,0}}{3c}\right)\left(\frac{1}{\phi_{\mathrm{act}}{}^{1/3}}\right) \frac{\left[1-\frac{1}{2}\left(\left.\frac{d\ln\phi}{d\ln\xi}\right|_{\mathrm{act}}\right)\right]^{2/3}}{\left[1-\frac{1}{3}\left(\left.\frac{d\ln\phi}{d\ln\xi}\right|_{\mathrm{act}}\right)\right]}, \tag{A.19}$$

with fractional error given by

$$\frac{\Delta r_{\mathrm{dry,c}}}{r_{\mathrm{dry,c}}} = \phi_{\mathrm{act}}{}^{1/3} \frac{\left[1-\frac{1}{3}\left(\left.\frac{d\ln\phi}{d\ln\xi}\right|_{\mathrm{act}}\right)\right]}{\left[1-\frac{1}{2}\left(\left.\frac{d\ln\phi}{d\ln\xi}\right|_{\mathrm{act}}\right)\right]^{2/3}} - 1\,. \tag{A.20}$$

In the Debye limit this fractional error can be approximated as

$$\frac{\Delta r_{\mathrm{dry,c}}}{r_{\mathrm{dry,c}}} \approx \frac{-1}{3}\left(\frac{K^2 r_{\sigma,0}}{3c^3 r_{\mathrm{dry}}}\right)^{3/4} = \frac{-4}{9}\left(\frac{\tilde{r}_{\mathrm{act}}}{r_{\mathrm{dry}}}\right)^{3/4}, \tag{A.21}$$

or in terms of the supersaturation s as Eq. (31):

$$\frac{\Delta r_{\mathrm{dry,c}}}{r_{\mathrm{dry,c}}} \approx \frac{-1}{3\cdot 2^{1/2}}\left(\frac{K}{c}\right)^{3/2} s^{1/2} = -\left(\frac{s}{\tilde{s}}\right)^{1/2}, \tag{A.22}$$

where $\tilde{s} \equiv 18(c/K)^3$ is approximately equal to 0.55 for ammonium sulfate and 4.4 for sodium chloride.

Title Captions

Fig. 1. Contours of constant fractional relative humidity h as a function of water activity a_w and dry radius r_{dry} (left panel) and contours of constant a_w as a function of h and r_{dry} (right panel), calculated from Eq. (1) for solution drops of ammonium sulfate and sodium chloride. Contours of $a_w = 0.99$ end at values of h corresponding to activation.

Fig. 2. Radius at $h = 1$, r_1, as a function of dry radius r_{dry} for solution drops of ammonium sulfate and sodium chloride, and values according to the Köhler model given by Eq. (11). Lower panel shows fractional error in r_1 (or in ξ_1) calculated from the Köhler model given by Eq. (27), and in the Debye limit given by Eq. (29).

Fig. 3. Radius at activation r_{act} as a function of dry radius r_{dry} for solution drops of ammonium sulfate and sodium chloride, and values according to the Köhler model given by Eq. (13a). Lower panel shows fractional error in r_{act} (or in ξ_{act}) calculated from the Köhler model and that in the Debye limit given by Eq. (30).

Fig. 4. Supersaturation at activation s_{act} as a function of dry radius r_{dry} for solution drops of ammonium sulfate and sodium chloride, and values according to the Köhler model given by Eq. (14a). Lower panel shows fractional error in s_{act} calculated from the Köhler model and in the Debye limit given by Eq. (A.18).

Fig. 5. Solution z (scaled radius ratio) to Eq. (16) for $h < 1$ as a function of scaled Kelvin factor ε. Also shown are the limiting solution and lowest-order correction for small ε, the

limiting solution for large ε, and approximate solution $(1+\varepsilon^{3/2})^{-1/3}$. Lower panel shows fractional error in the limiting and approximate solutions.

Fig. 6. Factors F_h, F_{K}, F_{R}, F_ξ, and F_ϕ quantifying the approximations made in deriving Eq. (8) as a function of fractional relative humidity h (for F_{h}) or water activity a_{w} (for other factors) for solution drops of ammonium sulfate (left) and sodium chloride (right). Each factor is equal to unity for abscissa equal to unity.

Fig. 7. Practical osmotic coefficient at $h = 1$, ϕ_1, as a function of dry radius r_{dry} for solution drops of ammonium sulfate and sodium chloride, and approximation given by Debye limit, Eq. (A.10).

Fig. 8. Practical osmotic coefficient at activation ϕ_{act} as a function of dry radius r_{dry} for solution drops of ammonium sulfate and sodium chloride, and approximation given by Debye limit, Eq. (A.11).

Fig. 9. Fractional error in radius ratio $\Delta\xi/\xi$, calculated from Eq. (34), as a function of fractional relative humidity h for bulk solution drops and for solution drops with r_{dry}/nm = 100, 50, 20, 10, and 5 of ammonium sulfate (top panel) and sodium chloride (bottom panel).

Fig. 1

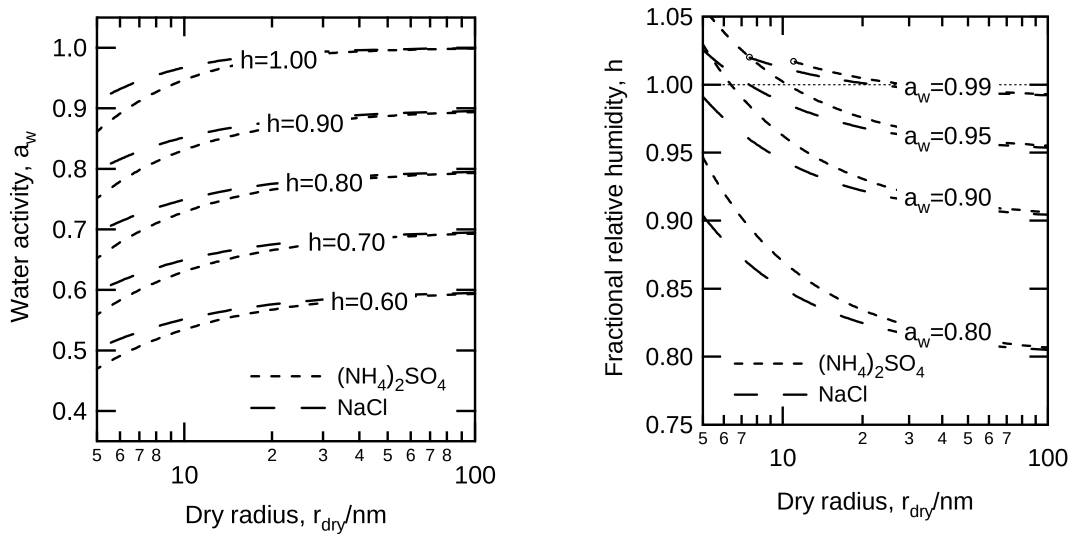

Fig. 1. Contours of constant fractional relative humidity *h* as a function of water activity a_w and dry radius r_{dry} (left panel) and contours of constant a_w as a function of *h* and r_{dry} (right panel), calculated from Eq. (1) for solution drops of ammonium sulfate and sodium chloride. Contours of $a_w = 0.99$ end at values of *h* corresponding to activation.

Fig. 2

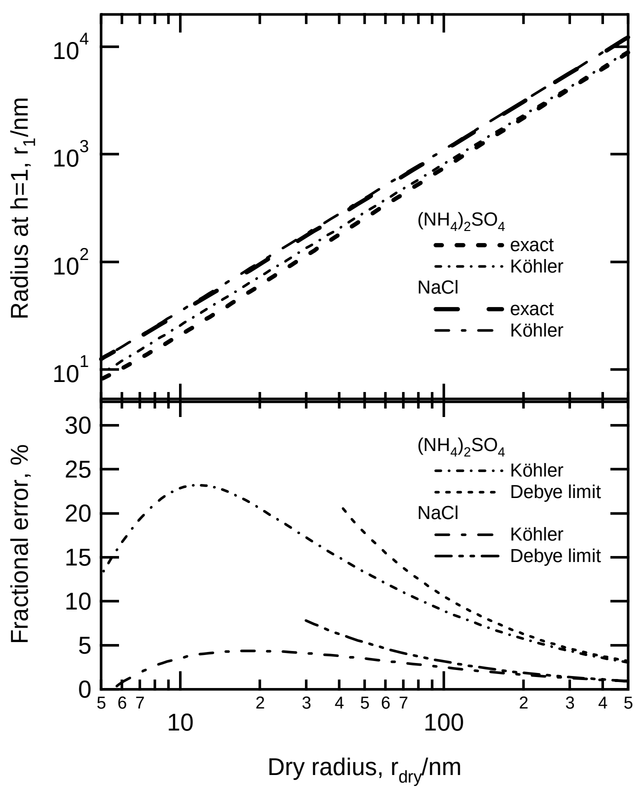

Fig. 2. Radius at $h = 1$, r_1, as a function of dry radius $r_{\rm dry}$ for solution drops of ammonium sulfate and sodium chloride, and values according to the Köhler model given by Eq. (11). Lower panel shows fractional error in r_1 (or in ξ_1) calculated from the Köhler model given by Eq. (27), and in the Debye limit given by Eq. (29).

Fig. 3

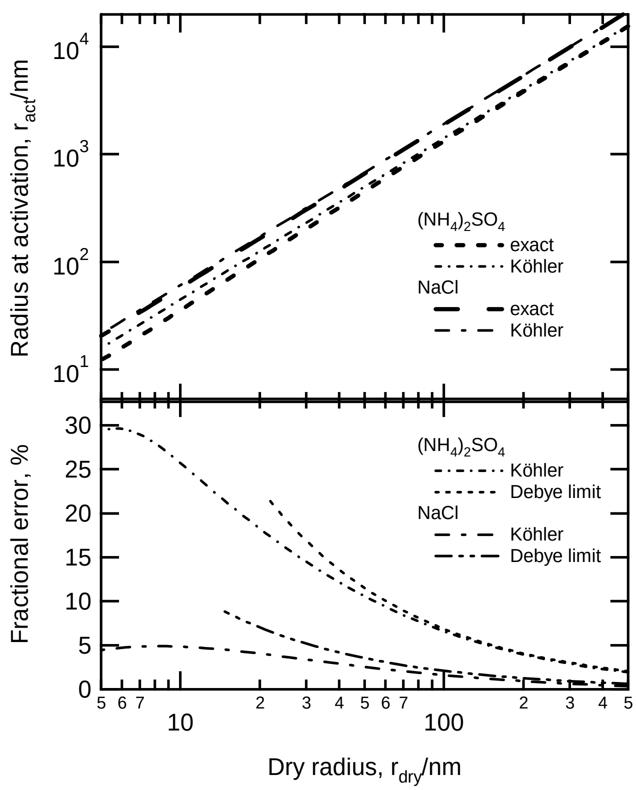

Fig. 3. Radius at activation r_{act} as a function of dry radius r_{dry} for solution drops of ammonium sulfate and sodium chloride, and values according to the Köhler model given by Eq. (13a). Lower panel shows fractional error in r_{act} (or in ξ_{act}) calculated from the Köhler model and that in the Debye limit given by Eq. (30).

Fig. 4

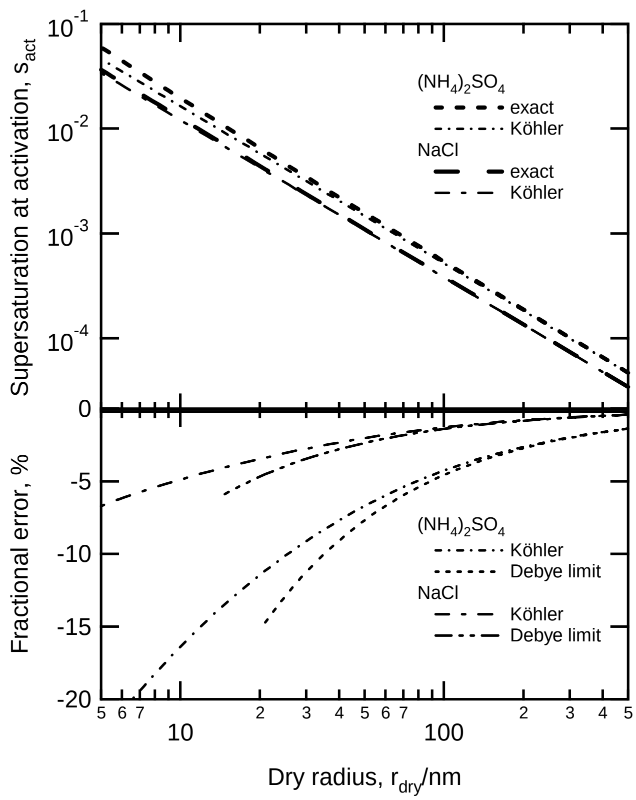

Fig. 4. Supersaturation at activation s_{act} as a function of dry radius r_{dry} for solution drops of ammonium sulfate and sodium chloride, and values according to the Köhler model given by Eq. (14a). Lower panel shows fractional error in s_{act} calculated from the Köhler model and in the Debye limit given by Eq. (A.18).

Fig. 5

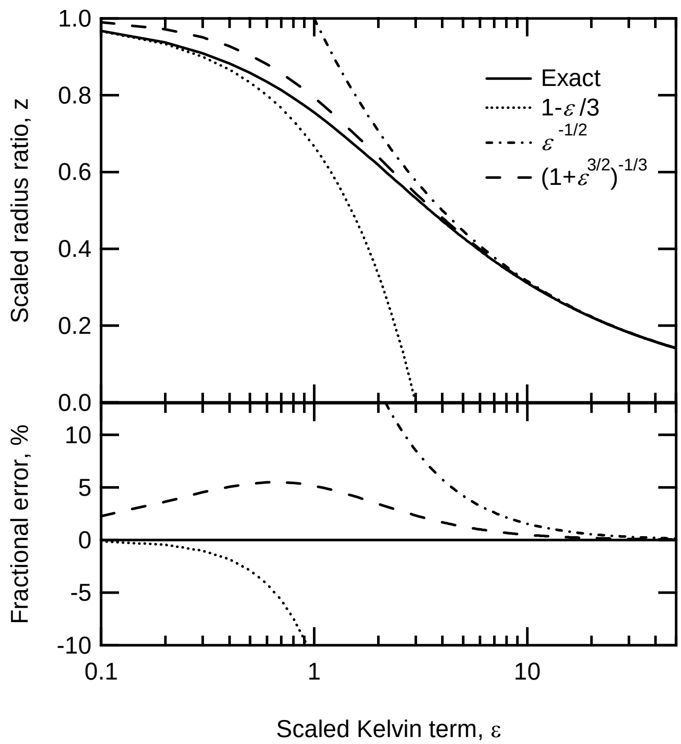

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Fig. 6

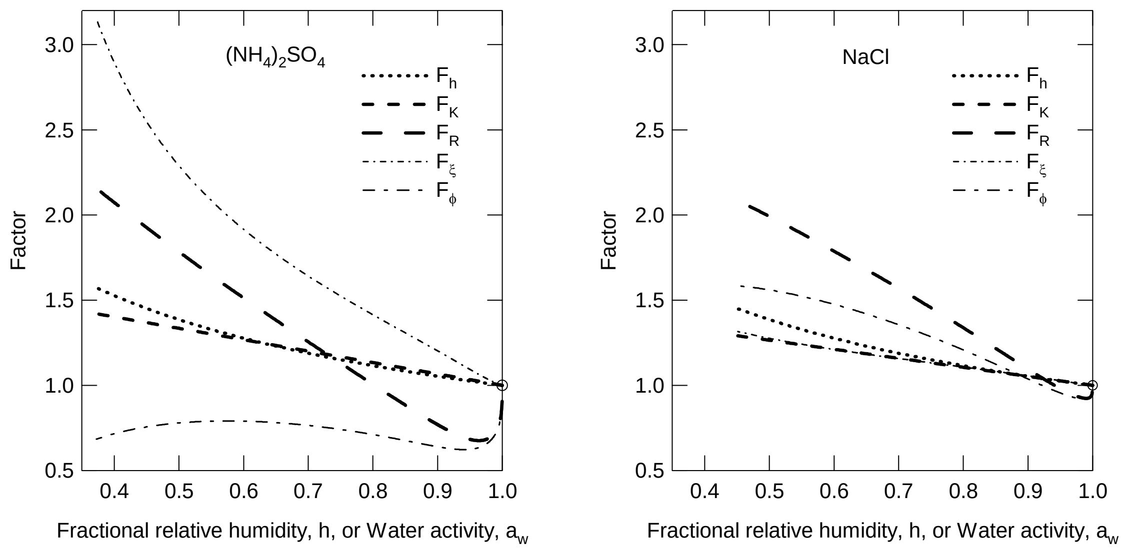

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Fig. 7

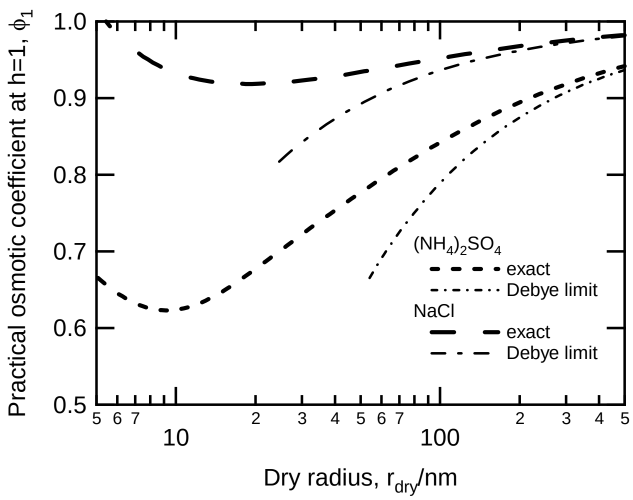


Fig. 7. Practical osmotic coefficient at $h = 1$, ϕ_1, as a function of dry radius r_{dry} for solution drops of ammonium sulfate and sodium chloride, and approximation given by Debye limit, Eq. (A.10).

Fig. 8

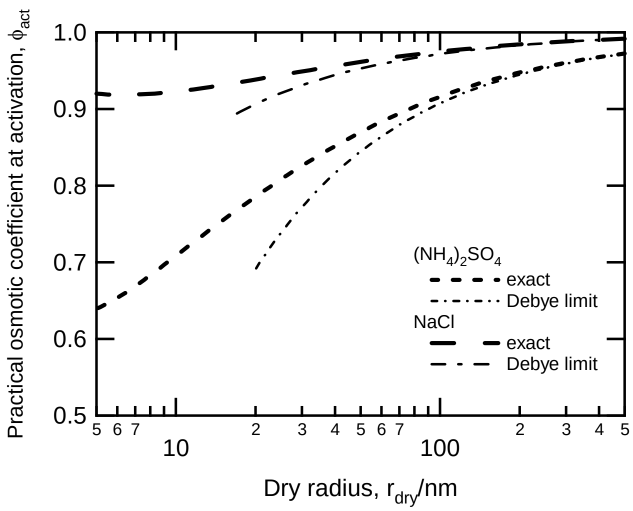
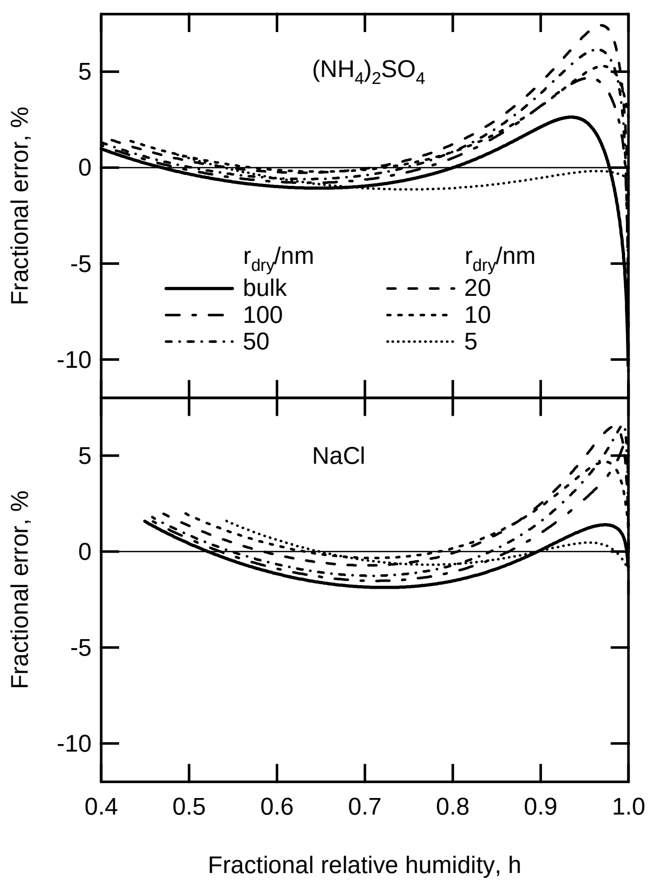


Fig. 8. Practical osmotic coefficient at activation ϕ_{act} as a function of dry radius r_{dry} for solution drops of ammonium sulfate and sodium chloride, and approximation given by Debye limit, Eq. (A.11).

Fig. 9



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